Supporting Information

In Situ Electrical Monitoring of Cation Exchange in Nanowires

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Experimental Details:

Samples: Electrodes were defined by optical lithography and consisted of a thermally evaporated 5nm titanium adhesion layer, a 75nm platinum layer, and a 20nm bismuth catalyst layer. For measurements correlating nanowire conductivity with elemental composition and optical absorption spectra we used interdigitated electrodes with a channel gap of 10μm and a channel length of about 55mm on fused silica substrates (12.5mmx12.5mmx0.5mm, MTI Corp.), see Fig.S1 a). Samples used for SEM structural analysis consisted of electrodes with a channel gap of 10μm and a channel length of 20μm on degenerately doped silicon substrates with a 300nm layer of insulating thermal oxide, see Fig.S1 b). The detailed procedure for the EC-SLS synthesis of CdSe nanowires as used for these experiments can be found in Dorn et al..[1] After nanowire synthesis, the samples were thoroughly cleaned in hexanes, before they were baked for 30min at 150ºC and for 30min at 350ºC under vacuum in a nitrogen atmosphere glove box. This step was found to greatly improve nanowire adhesion to the metal electrodes during the cation exchange process.

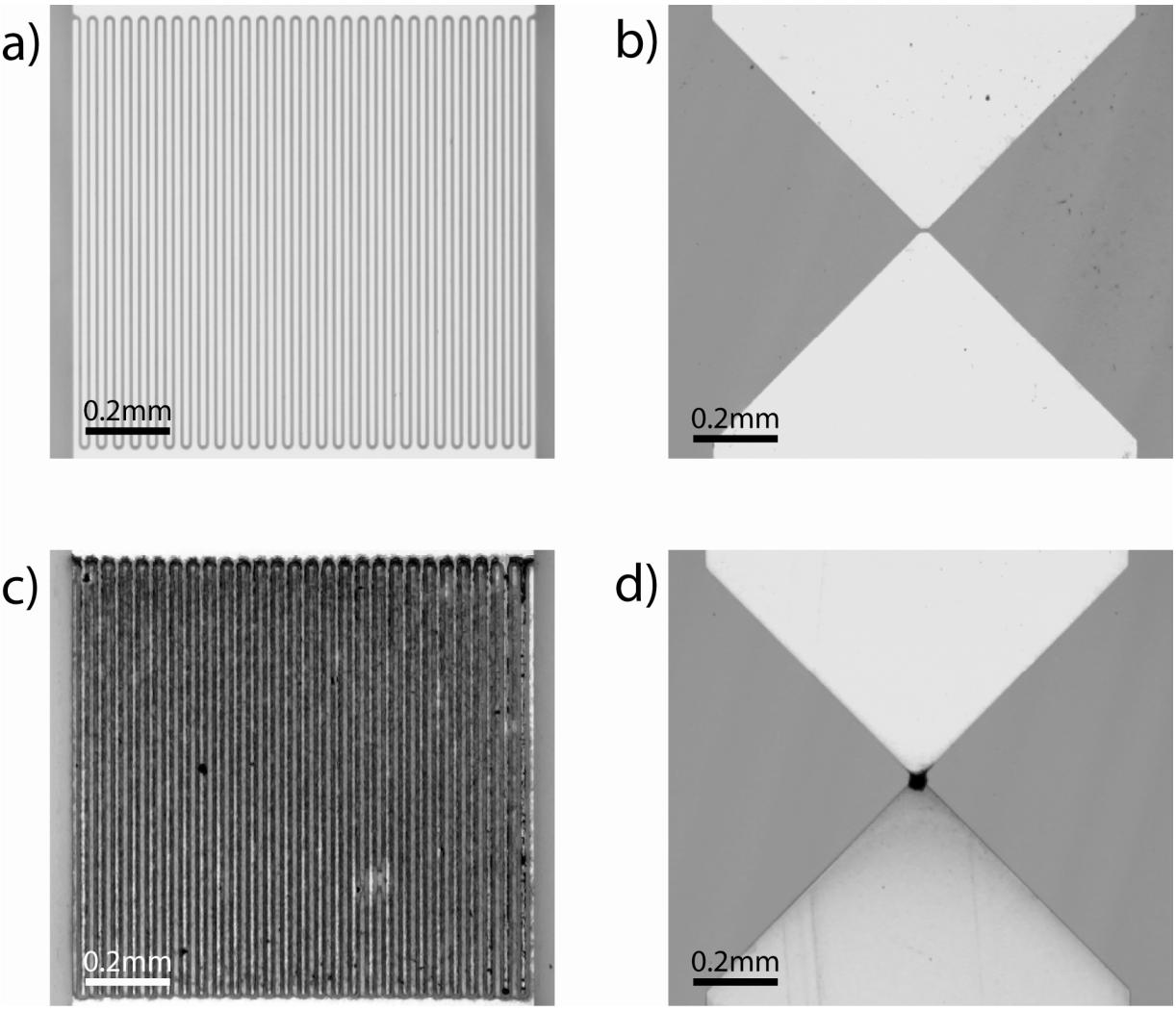

Figure S1, (a) Interdigitated electrode pair on fused silica, the channel width is about 10µm and the channel length is about 55mm. (b) Electrode pair on a doped silicon substrate with 300nm thermal oxide, the channel width is about 10µm and the channel length is about 20µm. (c) and (d) Electrode geometries as shown in (a) and (b) after nanowire growth by EC-SLS.

Cation exchange**:** The sample was immersed in a mixture of 10ml toluene and 40ml of methanol under ambient conditions. Cation exchange was initiated by injecting 100µl of 0.01M silver nitrate (99.9999%, Sigma Aldrich) in methanol solution.

Electrical measurements**:** We applied a bias with a DC voltage source (Yokogawa 7651 Programmable DC Source) and measured the resulting current either directly with a multimeter (Agilent 34401A) or in conjunction with a current/voltage converter (DL Instruments, LLC). In order to minimize electrochemical effects and to prevent silver dendrite formation, we typically measured the current for 3s at positive and negative bias and then turned off the voltage for 30-60s before recording the next current value.

Optical absorption measurements**:** We limited optical absorption to the actual device area with a 1mm diameter pinhole in a spectrometer (CARY 5000 UV-Vis-NIR). In order to eliminate contributions from the substrate or metal electrodes, spectra from a blank device before wire growth were used for baseline subtraction.

Additional structural characterization:

High resolution transmission electron microscope (HRTEM) images of CdSe nanowires (Fig.S2) and of Ag_2Se nanowires after complete cation exchange (Fig.S3) primarily show lattice fringes with a spacing of 0.35nm. This is consistent with topotaxial cation exchange from the wurtzite CdSe crystal structure to the orthorhombic or tetragonal crystal structures of room temperature β-Ag_2Se.

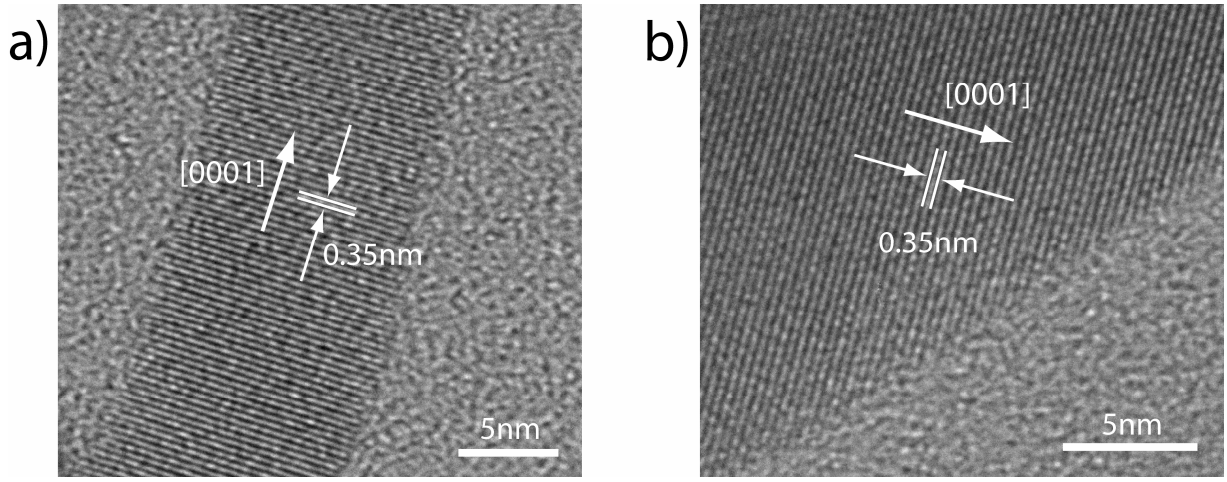

Figure S2, (a) and (b) High resolution transmission electron microscope (HRTEM) images of CdSe nanowires grown by EC-SLS. The lattice fringe spacing is consistent with values expected along the c-axis of wurtzite CdSe.

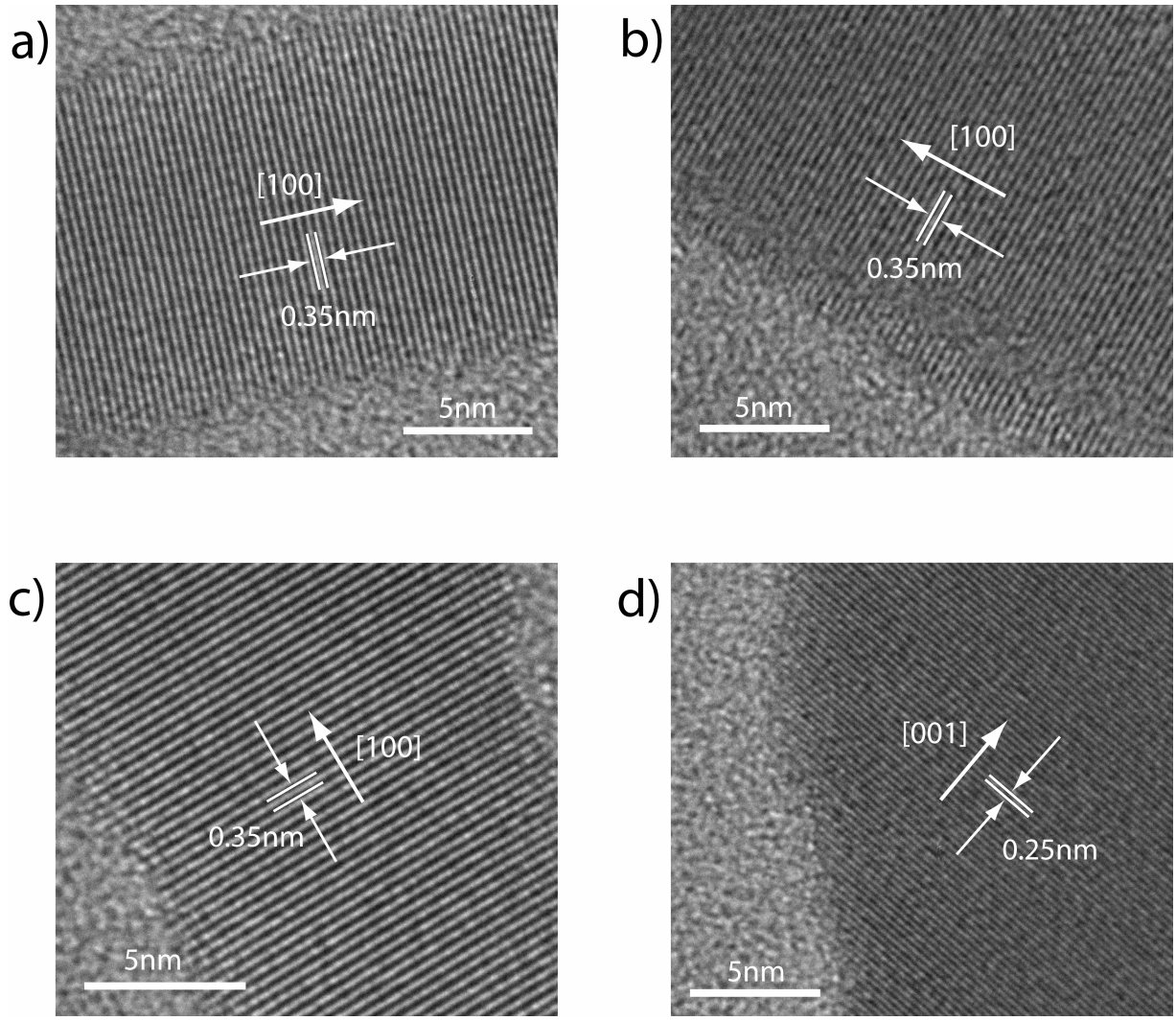

Figure S3, High resolution transmission electron microscope (HRTEM) images of Ag_2Se nanowires after complete cation exchange. The lattice fringes in (a), (b), and (c) are consistent with the spacing expected along the [100] axis of orthorhombic or tetragonal Ag_2Se. The lattice fringe spacing in (d) matches the [100] axis of tetragonal Ag_2Se.

Temperature dependent phase transition in Ag_2Se:

Since Ag_2Se is known to undergo a phase transition from the low temperature, semiconducting, β-phase to the high temperature metallic and superionic cubic α-phase around 120-140ºC, temperature dependent conductivity measurements can also serve as a probe for the structure of Ag_2Se. [2-4] Figure S4 shows temperature dependant

conductivity traces of a Ag_2Se nanowire sample immersed in octadecene. The two traces taken at different sweep rates closely overlap, which indicates a low time sensitivity of the effect and a high temperature dependent stability of the device. In addition, the temperature dependent phase transition from β- to α-Ag_2Se should not lead to a sudden change in wire length since the lattice constant in growth direction is the same for orthorhombic, tetragonal and cubic Ag_2Se nanowires. A sharp increase in conductivity upon heating is visible around 100ºC and a downward cusp during subsequent cooling occurs around 80ºC. This hysteretic temperature dependence is in good qualitative agreement with literature reports on single crystal and polycrystalline Ag_2Se samples. However, the transition temperature around 90ºC observed in our samples is lower than the values of 120-140ºC typically reported for bulk and thin film specimens. [2-4] The lower transition temperature in our samples lends additional weight to reports that the high temperature cubic phase of Ag_2Se is stabilized in the nanowire and nanocrystal geometries. [5,6] For some wire segments this could be the case even down to room temperature, [6] which would explain the conductivity offsets present below the transition temperature.

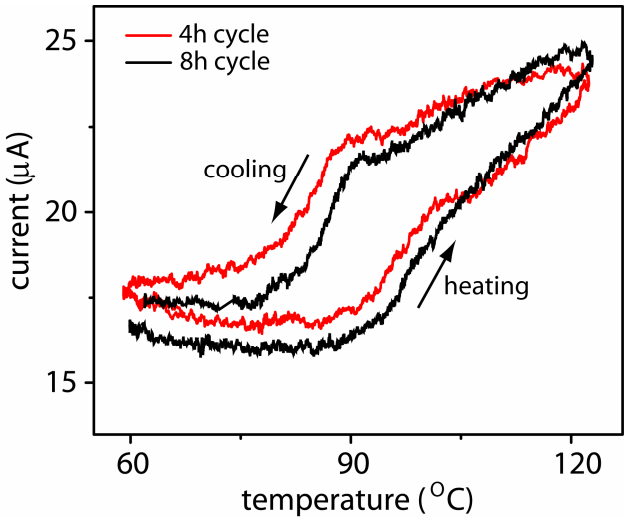

Figure S4. Current through a Ag_2Se nanowire mat as a function of temperature at a constant bias of 10mV.

References

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(4) Somogyi, K.; Safran, G. *Vacuum* **1995**, *46*, 1055-1058.

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(6) Schoen, D. T.; Xie, C.; Cui, Y. *Journal of the American Chemical Society* **2007**, *129*, 4116-+.